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Title: Interaction of gases on single-wall carbon nanotubes

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14. ABSTRACT

This project is a continuation of the earlier study on ?Interaction of water and methanol with single wall carbon nanotubes?. The objective of the project was to supplement previous work by considering (1) more than one molecule in the interaction, (2) extending the previous work by examining interactions with bundles of carbon nanotubes rather than a single nanotube, (3) comparing interactions within and between nanotubes, and (4) examining effects of nanotube deformation on the interaction. This study is to support the experimental work done using Raman spectroscopy by Prof. Maher Amar of Wright State University in association with Dr. John F. Maguire of the Air Force Research Laboratory.In general the interaction energies of H2O and CH3OH molecules on a (10,10) SWCNT, C60 and a graphene sheet are quite small (a few tens of meV) and it is weakly dependent on the orientation of the molecules. This is presumably due to the large HOMO-LUMO gap (6.2 and 5.58 eV (GGA) for water and methanol, respectively). The electronic structures (gap) of graphene, nanotubes and C60 differ and this could contribute to the differences. For (10,10) nanotube the interaction energy is more favorable outside (39 meV) the nanotube for water. This energy is significantly lower than the cohesive energy of water and therefore water is suggested to wet the nanotube because two molecules outside a nanotube form a dimer. The interaction energy for a dimer (see table below) also increases as compared to a single molecule. On the other hand for methanol the interaction energy for the two cases, outside as well as inside, is nearly the same, though the value remains small (40 meV). It is predicted that the competition between the molecules and molecule-nanotube wall could lead to interesting ordering in the nanotube which could depend on the size of the nanotube. The interaction energy on a C60 fullerene is significantly lower presumably due to its large HOMO-LUMO gap. The dependence of the interaction energy on gap seems to us a new finding and it would need further elaboration. Interestingly for graphene sheet the gap vanishes and the interaction energy increases. For water it has an intermediate value between C60 and (10,10) nanotube. However, the value of the interaction energy for methanol on graphene sheet increases to 60 meV. This is perhaps due to a more significant overlap of the molecular orbitals (molecule more flat than on nanotube) with those of the graphene sheet but it needs further clarification. The small values of the interaction energies indicate nearly negligible dependence on small deformation of the nanotubes resulting from bundle formation. A more significant effect could be due to changes in the electronic structure. However, this is again expected to be small due to weak interactions between the nanotubes. Much care has been taken to obtain these numbers. However, small differences resulting from orientational and positional changes could be there.

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Report on the Project

Interaction of Gases on Single Wall Carbon Nanotubes

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Introduction

This project is a continuation of the earlier study on "Interaction of water and methanol with single wall carbon nanotubes". The objective of the project was to supplement previous work by considering (1) more than one molecule in the interaction, (2)

extending the previous work by examining interactions with bundles of carbon nanotubes rather than a single nanotube, (3) comparing interactions within and between nanotubes, and (4) examining effects of nanotube deformation on the interaction. This study is to support the experimental work done using Raman spectroscopy by Prof. Maher Amar of Wright State University in association with Dr. John F. Maguire of the Air Force Research Laboratory.

Experimentally nanotubes are formed in a variety of diameters and chirality in the same sample. Prof. Amar has performed experiments also on fullerenes. It was discussed with Prof. Amar and Dr. Maguire to perform a study on C_{60} fullerene and a graphene sheet in order to understand the dependence of the interaction on the curvature of nanotube. Also C_{60} and graphene sheet systems on which experimental data can be very reliable as these can be produced with high purity. Single wall carbon nanotubes (SWCNT) could be metallic or semiconducting. Under experimental conditions, both types of nanotubes could be present. As the diameter of nanotube increases, the interaction of molecules will tend to show a behavior as on a graphene sheet. However, in small diameter nanotubes curvature could have significant effects. The change in the interaction of gases could be a measure that could be useful for applications of these materials as sensors. Calculations showed that in general the interaction of gases with nanotubes is weak and the deformation of nanotubes is very small effect. Accordingly the study on bundles and the effects of deformation was given low priority. Also there is a technical problem in dealing with interaction of water and other molecules with bundles. Calculations on SWCNT bundles using the generalized gradient approximation gave the spacing between

the nanotubes to be too large compared to experimental results. Treating the exchange-correlation energy within the local density approximation gives very good results. But, the local density approximation is not good to treat interaction of water. On the other hand GGA gives a good description of water interaction and a single nanotube. Therefore the emphasis of this study has been to obtain good treatment of water interaction with nanotubes.

The earlier study of the interaction of a molecule outside a nanotube was done by keeping nanotube in a cell with periodic boundary conditions. The separation between the nanotubes was varied by taking two different cell dimensions. The calculations showed weak interaction of molecules with a (10,10) nanotube, but significant variation on graphene and C_{60}. Further calculations of the interaction of molecules with a nanotube have now been done in a much larger unit cell and further detailed analysis has been carried out. These results provide a more consistent picture, and give an idea about the interaction of molecules between the nanotubes and among themselves. These are also presented here.

Method of calculations

The studies have been performed by doing first principles calculations in which electron-ion interaction is represented by the ultrasoft pseudopotentials. The plane wave method and generalized gradient approximation have been used to expand the wave function and

for the exchange-correlation energy, respectively. We considered interaction of a water molecule in detail on a graphene sheet, a C_{60} fullerene and a (10,10) single wall carbon nanotube (SWCNT) which is generally more abundant in samples. The accuracy of the calculations was tested by studying water, methane (CH_4) as well as a methanol (CH_3OH) molecules. CH_3OH differs from CH_4 in that one H is replaced by an OH group. The interaction energy in all cases is very weak and it is calculated to be of the order of a few tens of meV. It is due to the large highest occupied-lowest unoccupied molecular orbital (HOMO-LUMO) gaps in these molecules. The small values of the interactions require high accuracy and this made the convergence in calculations very time consuming. The dependence of the interaction on the orientation of the molecule also becomes weak. For nanotubes a large unit cell of square cross section with a side of 28 Å and with a repeat distance of about 4.92331 Å along the nanotube axis was taken. The nanotube was represented by 80 atoms with periodic boundary conditions and placed at the center of the cell. The molecule was placed along the diagonal of the square so that the interaction between the images could be negligible. 15 k-points were used along the nanotube axis to represent the Brillouin zone. Calculations were also done for a nanotube alone in the same unit cell with the energy cut-offs for the plane wave expansion as for O. Also calculations were done for a molecule as well as a dimer of water in the same unit cell to obtain the interaction energies. Similar calculations have been done on a C_{60} fullerene that was placed in a cube of 19Å side. In this case only the Γ-point was used to represent the Brillouin zone.

For graphene sheet, we considered periodic boundary conditions within the plane of the graphene sheet by considering 24 carbon atoms in the unit cell. A large number of atoms were necessary for the calculation of the interaction of molecules with graphene. Periodic boundary condition in the perpendicular direction was imposed by using vacuum space and a repetition distance of 12 Å. Water and methanol molecules were placed on the graphene sheet to calculate the interaction. The structural optimization was continued till the force on each ion became less than ~0.002 eV/Å. The Brillouin zone is represented by 4x4x2 **k**-points. The interaction energy has been calculated from E(Molecule) + E(system) – E(Molecule + system), where system is either a nanotube, fullerene or graphene sheet. Two calculations have been done for the molecules: 1) by considering the molecules in the same unit cell as the graphene sheet and using the same k-point integration mesh and 2) by taking a large unit cubic cell of 15 Å as well as 19Å side in order to identify interactions between the molecules. The latter calculations have been done with Γ point in the **k**-space. Small variation in values can be expected due to a difference in the grids in the reciprocal space (not exactly proportionate) in the two cases

Results

A. Interaction of Gases with Nanotubes

H_2O

The converged structures of a (10,10) SWCNT and a water molecule interacting with it *outside* is shown in Figs. 1a and b, respectively. Water molecule interacts with H pointing towards a carbon atom in the SWCNT. The C-H bond length is about 2.79 Å. For calculating the binding energy of a water molecule on (10,10) SWCNT, further calculation of the energy of a water molecule is needed. For this purpose the gas

molecule (water and also other molecules) were kept at the same position as on a nanotube. The same procedure of calculation was repeated and the structure was optimized. As the separation between the molecules along the nanotube axis is relatively small, there is a weak interaction between the gas molecules. Compared with an independent calculation of an isolated gas molecule placed in a large simple cubic box, this interaction energy is about 45 meV. The interaction energy of a water molecule on (10,10) SWCNT is about 39 meV. The earlier calculated value was about 86 meV which was with reference to the energy of an isolated water molecule. The difference is

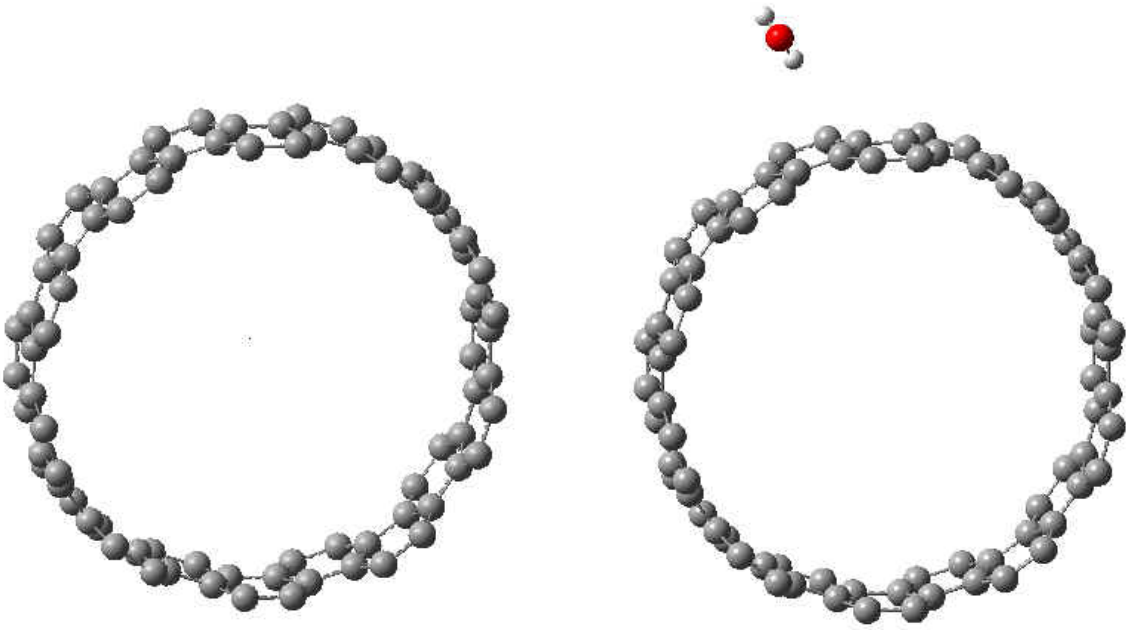


Fig. 1. (a) (10,10) single wall carbon nanotube, (b) a water molecule interacting with (10,10) SWCNT (outside). Red (white) ball represent oxygen (hydrogen) atoms.

due to the interaction between the water molecules in neighboring cells (that was not corrected in the earlier report). Also the earlier calculations were done in a different unit

cell and the accuracy of the present calculations is much better. However, only a small difference in values (about 2 meV) indicates good accuracy of the earlier calculations. A water molecule inside a nanotube (Fig. 2a) has a binding energy of 29 meV. In this case water molecule is shifted towards the wall of the nanotube but the nearest separation between H atom of the molecule and the nanotube is large (~ 4.11 Å). *Therefore, the behavior of a water molecule inside a nanotube is quite different from the one found outside the nanotube.* Our calculations suggest that though water molecules has a binding energy inside the nanotubes, it has a preference to bind outside of a nanotube. A longer distance could be due to the higher charge density arising from the curvature at the same distance as outside the nanotube. Here it is interesting to note that the interaction between a water dimer is about 100 meV per molecule and this value will be more in the case of liquid water. Therefore, the possibility of water inside will depend also on the diameter of the nanotube.

When two water molecules are brought near a nanotube, there is water dimer formation with one H lying at 2.61 Å from near a top position on the nanotube. An interesting observation is that one H of one water molecule points towards the nanotube but the other water molecule lies nearly flat on the nanotube (see Fig. 2b). The O-H (hydrogen bonded) separation between the water molecules is 1.90 Å which is close to the value in isolated water dimer. *This result suggests that when many water molecules interact with a*

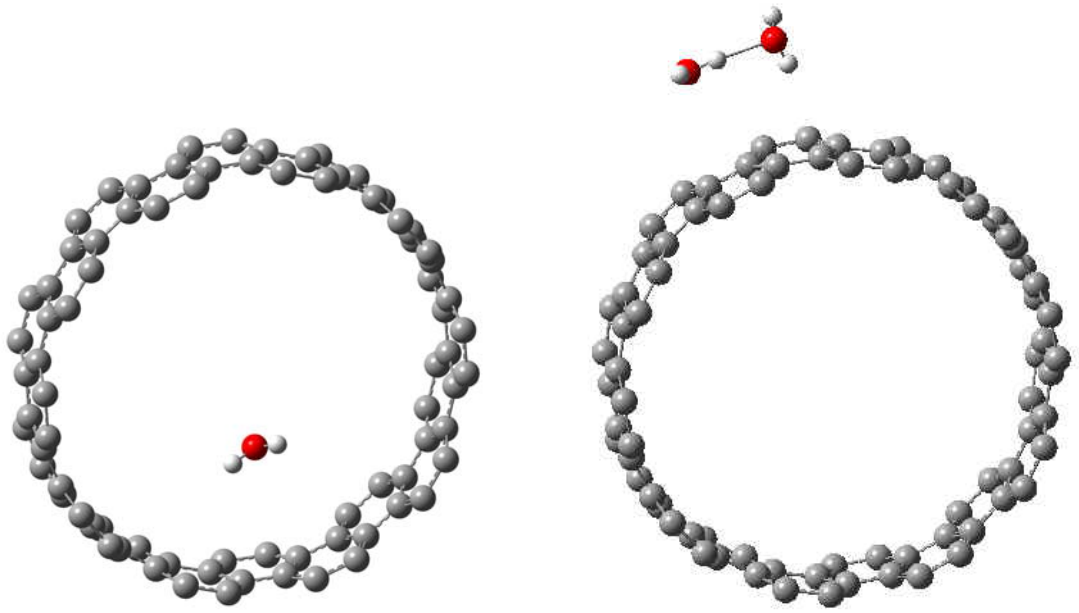


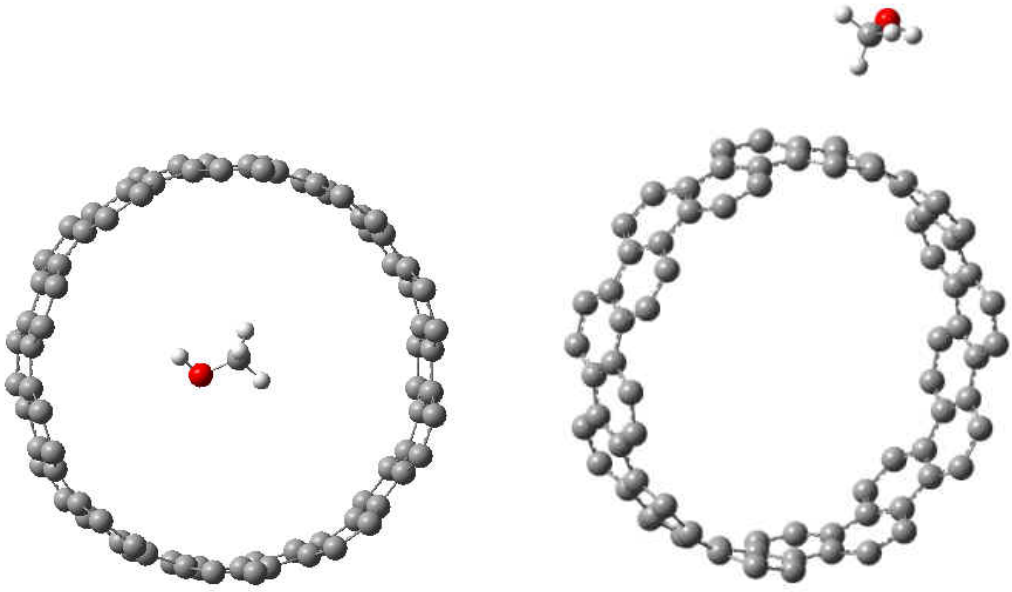
Fig. 2. (a) A water molecule inside a (10,10) nanotube, (b) a water dimer interacting outside a (10,10) nanotube. Red balls are oxygen atoms while white balls are hydrogen atoms.

nanotube, each molecule may not have optimal interaction with the nanotube. There is a competition between the interaction with the nanotube and the interaction between the water molecules. Furthermore, there is a small decrease in the C-H bond length. As compared to a single water molecule, the binding energy per water molecule for the case of a dimer is 44 meV. This value has been obtained by separately calculating the value of the energy of a dimer (optimized) in the same unit cell. The resulting interaction energy is slightly more than the value for a single water molecule (39 meV). Therefore, there is a small increase in the interaction energy on (10,10) nanotube from ~39 meV to around 44 meV per water molecule. Therefore more water molecules are favored around a nanotube. As interaction between the water molecules is more significant (compare with about 100

meV per molecule for a dimer), it is concluded that a nanotube would be wet by water. Further the above mentioned values may have a small variation depending on the orientation of the molecules as well as the position of the molecule on the nanotube.

CH_3OH

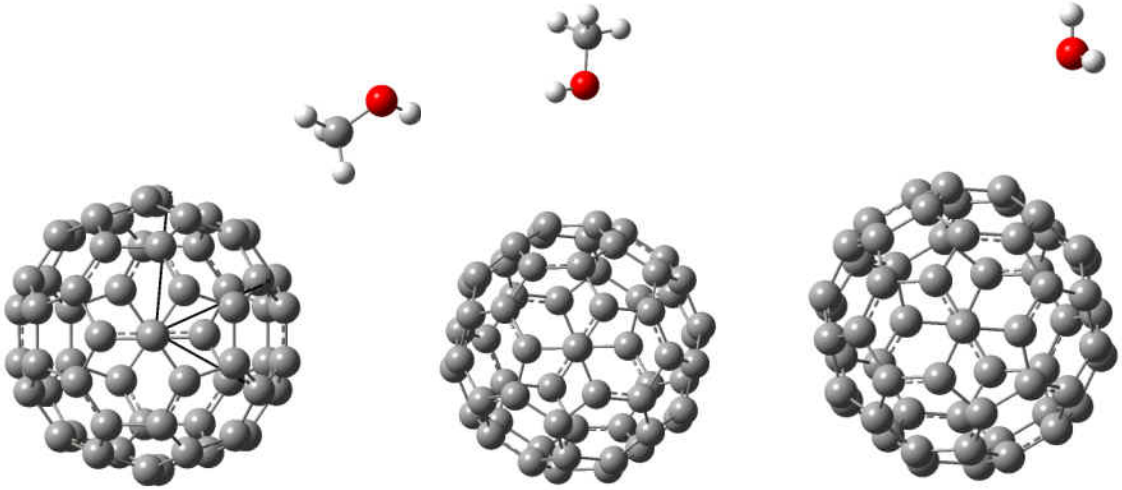
Similar to a water molecule, calculations have been done on a methanol molecule inside and outside a (10,10) SWCNT (Fig. 3). The interaction energy of methanol outside a (10,10) SWCNT is about 40 meV, almost nearly the same as for a water molecule. The interaction of methanol is also via an H atom and the C-H bond length is about 3.42 Å which is slightly more than the value for water. When a methanol molecule is placed inside a (10,10) nanotube, it drifts towards the wall of the SWCNT and the interaction energy is about 41 meV. This value is more than in the case of a water molecule. It is suggested that a higher value of the interaction energy is due to bigger size of the molecule so that interaction of other atoms in the molecules is more than in the case of a water molecule. Similar to H_2O, *the nearest distance to the nanotube wall is about 4.48 Å which is significantly longer than the value outside the nanotube*. Therefore again methanol molecule behaves differently inside a (10,10) nanotube than outside though the interaction energy is nearly the same.



CH_3OH inside (10,10) nanotube 41 meV CH_3OH outside (10,10) 40 meV

B. Interaction of gases on C_{60} fullerene

The optimized structures for interaction of water and methanol on C_{60} are shown in Fig. 4.



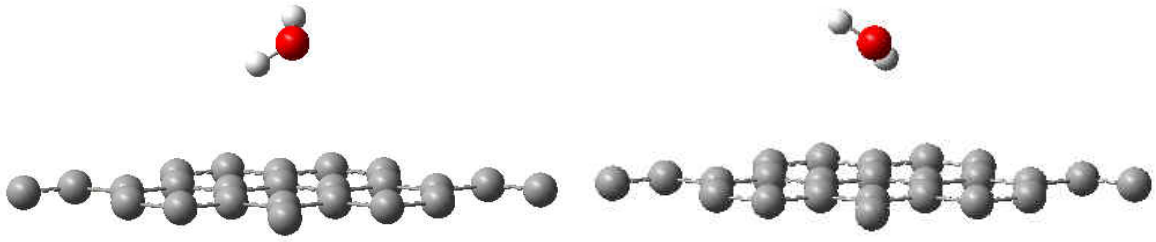
CH_3OH, 23 meV CH_3OH, 23 meV H_2O, 22 meV

Fig. 4. Converged atomic structures of CH_3OH and H_2O molecules interacting with C_{60}. For methanol two configurations have been shown with H or O towards C_{60}.

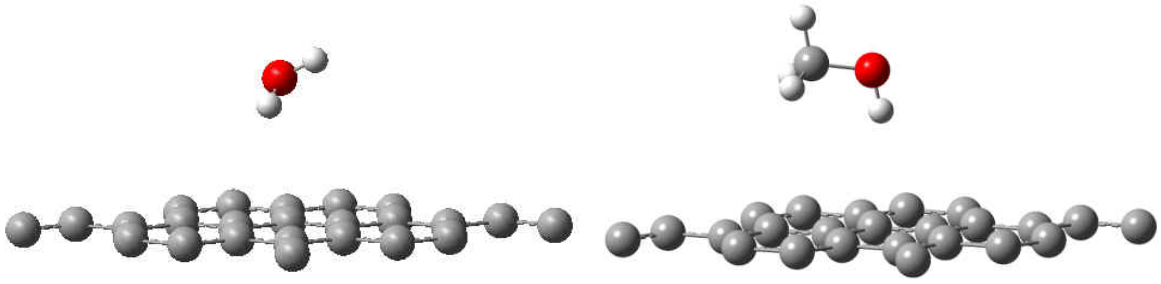
The interaction energy of water or methanol molecule on C_{60} is nearly the same and does not depend significantly on the orientation of the molecule. The interaction energy is slightly lower (22 and 23 meV for water and methanol, respectively) compared with a (10,10) nanotube. This is likely to be due to the large (1.65 eV) HOMO-LUMO gap (GGA) in C_{60}. Slightly larger value for methanol is consistent with the nanotube result. Furthermore the nearest separation of the H_2O (CH_3OH) molecule from the C_{60} is 4.08 (4.06 Å) which is significantly longer than the value for inter-fullerene or inter-nanotube separation in bundles. We considered another configuration of CH_3OH in which three H atoms pointed towards the C_{60} and in this case the nearest separation is about 3.26 Å which is nearly the same as the separation between fullerenes in solid C_{60} and nanotubes in a bundle. In both cases the interaction is very weak and has nearly the same value.

C. Interaction of gases with graphene

We considered a few initial configurations of the molecules on graphene sheet. Results from three configurations of H_2O are shown and in all cases the energies are similar with H pointing down. This result is similar to the one obtained on nanotubes. The interaction energy is calculated by subtracting the energy of the optimized molecule in the same unit



Initially both H pointing down 33 meV Initially O pointing down 31 meV



Initially H_2O flat on the sheet 28 meV CH_3OH 60 meV

cell. The interaction energy for water is rather low (~ 30 meV) but it is nearly twice for a methanol molecule. The nearest distance for water (methanol) molecule from the sheet is 3.20 (2.73) Å. This result differs from the nanotube case as the nearest distance from nanotube for H_2O was 2.61 Å while for methanol molecule it was longer. This is an anomalous result and the source of this difference is not yet clear.

Conclusions

In general the interaction energies of H_2O and CH_3OH molecules on a (10,10) SWCNT, C_{60} and a graphene sheet are quite small (a few tens of meV) and it is weakly dependent on the orientation of the molecules. This is presumably due to the large HOMO-LUMO gap (6.2 and 5.58 eV (GGA) for water and methanol, respectively). The electronic structures (gap) of graphene, nanotubes and C_{60} differ and this could contribute to the differences. For (10,10) nanotube the interaction energy is more favorable outside (39 meV) the nanotube for water. This energy is significantly lower than the cohesive energy of water and therefore water is suggested to wet the nanotube because two molecules outside a nanotube form a dimer. The interaction energy for a dimer (see table below)

also increases as compared to a single molecule. On the other hand for methanol the interaction energy for the two cases, outside as well as inside, is nearly the same, though the value remains small (40 meV). It is predicted that the competition between the molecules and molecule-nanotube wall could lead to interesting ordering in the nanotube which could depend on the size of the nanotube. The interaction energy on a C_{60} fullerene is significantly lower presumably due to its large HOMO-LUMO gap. The dependence of the interaction energy on gap seems to us a new finding and it would need further elaboration. Interestingly for graphene sheet the gap vanishes and the interaction energy increases. For water it has an intermediate value between C_{60} and (10,10) nanotube. However, the value of the interaction energy for methanol on graphene sheet increases to 60 meV. This is perhaps due to a more significant overlap of the molecular orbitals (molecule more flat than on nanotube) with those of the graphene sheet but it needs further clarification. The small values of the interaction energies (see table below) indicate nearly negligible dependence on small deformation of the nanotubes resulting from bundle formation. A more significant effect could be due to changes in the electronic structure. However, this is again expected to be small due to weak interactions between the nanotubes. Much care has been taken to obtain these numbers. However, small differences resulting from orientational and positional changes could be there. We would expect the interaction energies given here to be good representative of the interaction of a water and methanol on these systems.

Table: The calculated interaction energies.

	C_{60}	(10,10) Nanotube		Graphene
		Outside	Inside	
CH_3OH	23 meV	40 meV	41 meV	60 meV
H_2O	22 meV	39 meV	29 meV	30 meV

Interaction energy of a water dimer on (10,10) nanotube = 44 meV per water molecule

Publications

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